

PATENT ABSTRACTS OF JAPAN

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(54) CYANATE ESTER-COPREPOLYMER

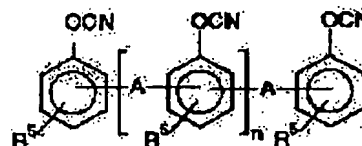
(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject co-prepolymer slight in drop of its heat resistance even if used through mixing with an epoxy resin or the like by prepolymerizing a specific cyanate ester followed by addition of a specific compound to conduct a further prepolymerization.

SOLUTION: This co-prepolymer is obtained by prepolymerizing (A) a bifunctional cyanate ester of formula I (R1 and R2 are each H or a ≤ 6 C alkyl, or bound to each other to form a cycloalkyl; R3 and R4 are each H, a halogen or a ≤ 6 C alkyl) (pref. a bisphenol A-type cyanate ester) followed by addition of a multifunctional cyanate ester of formula II ((n) is 0.5-3; R5 is H, a halogen or a ≤ 6 C alkyl; A is methylene or dicyclopentadienyl) (pref. a phenol novolak-type cyanate ester) in such an amount as to account for 30-60 wt.% of the final co-prepolymer to conduct a further prepolymerization.



I



II

AN 2000:470412 HCAPLUS
DN 133:90210
ED Entered STN: 12 Jul 2000
TI Cyanate ester copolymers and their blends with other resins
IN Hagiwara, Isao; Ishii, Kenji; Yamazaki, Katsutoshi
PA Mitsubishi Gas Chemical Co., Ltd., Japan
SO Jpn. Kokai Tokkyo Koho, 9 pp.
CODEN: JKXXAF

DT Patent
LA Japanese
IC ICM C08G073-06
ICS C08G059-40; C08L063-00; C08L079-04
CC 37-3 (Plastics Manufacture and Processing)
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2000191776	A	20000711	JP 1998-366855	19981224 <--
PRAI	JP 1998-366855		19981224		

AB The copolymers giving resin blends with good retention of heat resistance and adhesion to Cu foil, etc., useful for circuit board laminates, are obtained by pre-polymerizing a bisphenol type dicyanate ester, then adding a polyphenol polycyanate ester having >3 cyanate groups and polymerizing. Thus, heating 1000 parts Skylex CA 200 (bisphenol A dicyanate) at 135-145° for 6 h gave a prepolymer with number-average mol. weight (Mn) 1570, and weight-average mol. weight (Mw) 5460, 500 parts of which was heated with parts PT 30 (phenolic novolak cyanate ester) at 135-145° for 3 h to give a copolymer with Mn 1870 and Mw/Mn 5.8. Dissolving the copolymer 30 with Sumiepoxy ESCN 220F (cresol novolak epoxy resin) 50 and Epikote 828 20 in MEK 200, and mixing the resulting solution with Zn octanoate 0.01 part gave a varnish, in which glass cloths were impregnated, dried, and heated at 170° for 150 s to give B-stage prepregs. A Cu-clad laminate containing 4 layers of the prepregs was prepared which showed peel strength 1.1 kN/cm², viscoelasticity 2.63x10⁷ and 1.35x10⁷ P at 150° and 260°, resp., and good resistance to solder heat test.

ST heat resistance prepreg laminate cyanate resin compn; bisphenol dicyanate novolak cyanate copolymer heat resistance; epoxy resin crosslinking cyanate copolymer resin; copper foil adhesion cyanate copolymer resin; glass cloth prepreg laminate polycyanurate; circuit board laminate epoxy polycyanurate resin

IT Heat-resistant materials
Printed circuit boards
(cyanate ester copolymers and blends with other resins for use in circuit board laminates)

IT Polycyanurates
Polycyanurates
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(epoxy; cyanate ester copolymers and blends with other resins)

IT Reinforced plastics
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(glass fiber-reinforced; cyanate ester copolymers and blends with other resins for use in circuit board laminates)

IT Epoxy resins, preparation
Epoxy resins, preparation
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(polycyanurate-; cyanate ester copolymers and blends with other resins)

IT Polycyanurates
RL: POF (Polymer in formulation); RCT (Reactant); RACT (Reactant or reagent); USES (Uses)

(polyphenol-based, reactant; cyanate ester copolymers and blends with other resins)

IT 282117-96-8P 282117-97-9P 282117-98-0P 282118-00-7P

RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)

(cyanate ester copolymers and blends with other resins for use in circuit board laminates)

IT 282117-94-6P 282117-95-7P

RL: IMF (Industrial manufacture); POF (Polymer in formulation); RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent); USES (Uses)
(prepolymer; cyanate ester copolymers and blends with other resins)

DERWENT-ACC-NO: 2000-630483

DERWENT-WEEK: 200064

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TITLE: Cyanate co-prepolymer with at least two kinds of
cyanates having improved physical properties for use in
production of prepreg and PCB

PATENT-ASSIGNEE: MITSUBISHI GAS CHEM CO INC[MITN]

PRIORITY-DATA: 1998JP-0366855 (December 24, 1998)

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APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2000191776A	N/A	1998JP-0366855	December 24, 1998

INT-CL (IPC): C08G059/40, C08G073/06, C08L063/00, C08L079/04

ABSTRACTED-PUB-NO: JP2000191776A

BASIC-ABSTRACT:

NOVELTY - A cyanate co-prepolymer is prepared by forming prepolymer of bifunctional cyanate, and then by adding polyfunctional cyanate.

DETAILED DESCRIPTION - A cyanate co-prepolymer is prepared by forming prepolymer of bifunctional cyanate of formula (1), and then by adding polyfunctional cyanate of formula (2).

R1, R2 = H or straight chain or branched upto 6C alkyl; or R1+R2 completes a ring;

R3, R4 = H, halogen, or straight chain or branched up to 6C alkyl;

n = positive number of 0.5-3; R5 = H, halogen or straight chain or branched up to 6C alkyl;

A = methylene or dicyclopentadienyl.

An INDEPENDENT CLAIM is also included for a thermosetting resin composition consisting of the cyanate.co-prepolymer and a thermosetting resin.

USE - The cyanate.co-prepolymer is suitable for coatings, moldings, adhesives, a printed circuit board and insulating material. The thermosetting resin composition is suitable for prepreg. The prepreg is suitable for a metal foil-lined laminates.

ADVANTAGE - The co-prepolymer has improved physical properties. The thermosetting resin composition consisting of the co-prepolymer and an epoxy resin has good operating properties, thermoresistance, electrical characteristics and physical characteristics.

CHOSEN-DRAWING: Dwg.0/4

TITLE-TERMS: CYANATE CO PREPOLYMER TWO KIND IMPROVE PHYSICAL PROPERTIES PRODUCE
PREPREG PCB

DERWENT-CLASS: A21 A85 G02 G03 L03

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the KOPURE polymer of the cyanic-acid ester manufactured by the specific approach using two or more sorts of cyanic-acid ester. As compared with the former, the coating excellent in operability, thermal resistance, the electrical property, the physical characteristic, etc., mold goods, adhesives, a printed wired board, an insulating material, etc. are obtained, and the obtained KOPURE polymer can be widely applied to an electronics application, when it uses combining an epoxy resin etc.

[0002]

[Description of the Prior Art] As current and SHIANATO resin, the cyanic-acid ester compound of the bisphenol A mold is used, and it is mainly known that this hardened material has high thermal resistance. However, the resin which hardened the above-mentioned cyanic-acid ester independently is used as a constituent mixed with the bismaleimide resin, the epoxy resin, etc. according to the need property from viewpoints, like it is generally weak and adhesion with copper foil is low. Consequently, the hardened material of the constituent mixed with other resin was resin with which thermal resistance fell somewhat rather than the independent hardened material of the above-mentioned bisphenol A mold cyanic-acid ester.

[0003] Moreover, the constituent with which are satisfied of many properties required of the resin for laminates, for example, adhesion with copper foil, and the stability (pressure cooker test-CT) under moisture absorption is not found out, and the cyanic-acid ester of a phenol novolak mold is not used as resin for laminates, although it is known rather than the cyanic-acid ester of the bisphenol A mold that it is a high heatproof. In recent years, electronics each field followed on developing, high performance-ization was called for more, in the laminate field, it is a nearby high heatproof and development of cyanic-acid ester with many other good physical properties was desired.

[0004]

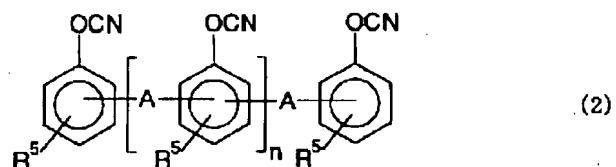
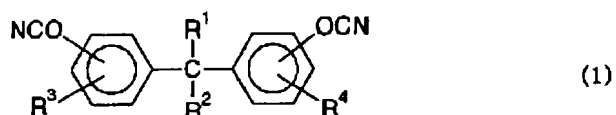
[Problem(s) to be Solved by the Invention] even if it uses it, performing this invention in view of the above troubles, and mixing with resin, such as an epoxy resin, -- heat-resistant lowering -- few -- in addition -- and it is in offering the new cyanic-acid ester prepolymer which can also maintain properties, such as dielectric characteristics, adhesion with copper foil, and PCT thermal resistance.

[0005]

[Means for Solving the Problem] That is, this invention is the following general formula (1). The following general formula after prepolymer-izing 2 organic-functions cyanic-acid ester shown (2) It is cyanic-acid ester Co-op REPORIMA obtained by adding the polyfunctional cyanic-acid ester shown and prepolymer-izing further.

[0006]

[Formula 2]



(In a formula (1), you may differ, it is that R1 and R2 are the same, or a hydrogen atom, a straight chain, a with a branched carbon number of six or less alkyl group or the cycloalkyl that R1 and R2 combined, and R3 or R4 are a hydrogen atom, a halogen atom, a straight chain, or the with a carbon number of six or less branched alkyl group.) Formula (2) It sets and is n. 0.5-3 A positive number is expressed, R5 is a hydrogen atom, a halogen atom, a straight chain, or the with a carbon number of six or less branched alkyl group, and A is a methylene group or a dicyclopentadienyl radical.

[0007] At this invention, it is this general formula (1). 2 organic-functions cyanic-acid ester shown is bisphenol A mold cyanic-acid ester, and it is this general formula (2). It is desirable that the polyfunctional cyanic-acid ester shown is phenol novolak mold cyanic-acid ester, and it is this general formula (2). It is desirable that the amount of the polyfunctional cyanic-acid ester used shown is 30 - 60% of cyanic-acid ester Co-op REPORIMA. Moreover, this general formula (1) Prepolymer-ization of 2 organic-functions cyanic-acid ester shown It is desirable that 20 - 60% of the cyanate group contained in raw material cyanic-acid ester makes it react. Furthermore, this general formula (1) To the prepolymer of this 2 organic-functions cyanic-acid ester shown, it is this general formula (2). It is desirable to make 10 - 50% of the cyanate group in which prepolymer-ization performed by adding the polyfunctional cyanic-acid ester shown exists in the condition of having added react.

[0008] And cyanic-acid ester Co-op REPORIMA of this invention gives a good thermosetting resin constituent combining the resin which can heat-harden, especially an epoxy resin. This thermosetting resin constituent is suitably used for a reinforcement base material as impregnation and a metallic foil tension laminate which dries, and is made into prepreg and comes to carry out laminate molding of this prepreg and the metallic foil.

[0009] Hereafter, the configuration of this invention is explained. General formula which this invention described above (1) Although it can be used without being limited especially if it is the compound which has two cyanate radicals in 1 molecule as 2 organic-functions mold cyanic-acid ester shown, the cyanic-acid ester of a bisphenol mold is desirable. The cyanic-acid ester of easy bisphenol A of acquisition is suitable especially. Moreover, general formula (2) Although it can be especially used without a limit if it is the compound which has three or more cyanate radicals as the average in 1 molecule as cyanic-acid ester of the three or more organic functions many organic functions shown It is easy and suitable phenol novolak mold cyanic-acid ester -- acquisition -- Furthermore, since the average n of a repeat unit may gel in the phase which a small thing has a small contribution of heat-resistant improvement, and n makes a prepolymer at reverse in being not much large, it is n. 0.5-3 A thing is suitable.

[0010] Next, the process of cyanic-acid ester Co-op REPORIMA of this invention is explained. General formula (1) It is a general formula (2) about bisphenol A cyanic-acid ester as 2 organic-functions mold cyanic-acid ester. The case where phenol novolak mold cyanic-acid ester is used as polyfunctional cyanate is explained.

[0011] Temperature (it is described as "Prepolymer A" below.) is manufactured for bisphenol A cyanic-acid ester. A cyanate group is made to react, carrying out melting and stirring in 100 - 180 **, and it is the prepolymer of bisphenol A cyanic-acid ester. In this prepolymer-ized reaction, a catalyst may be used if needed. As a catalyst, it is metal salt; triethylenediamines, such as organometallic compound; aluminum chlorides, such as octylic acid zinc, tin octylate, dibutyl tin dimaleate, and iron <3> acetylacetonate, tin chloride, and a zinc chloride, dimethyl benzylamine, and 2. - Amines, such as a

methyl imidazole; phenols, such as a phenol and a catechol, etc. are mentioned and, generally a well-known thing can be used as a curing catalyst of cyanic-acid ester. Moreover, the above-mentioned catalyst may combine one sort or two sorts or more. Although it cannot generally specify from changing with classes of catalyst as an amount of the catalyst which can be added, generally 2% or less is enough. [0012] By the reaction of the above-mentioned prepolymer-izing, a part of cyanate group of bisphenol A cyanic-acid ester causes 3 quantification reactions, and it generates a triazine ring. Since it will gel if this 3 quantification reaction advances too much, and it becomes insoluble at a solvent, it cannot be used as a prepolymer A. Therefore, as conversion of a cyanate group, 10 - 70% is desirable, and 20 - 60% is suitable. The conversion of a cyanate group is a cyanate group in infrared spectrometer (IR). (2270cm⁻¹) Triazine ring (1370cm⁻¹) Absorption peak of the benzene ring origin which does not change absorption peak reinforcement at a reaction (for example, 1500cm⁻¹) It can be made criteria and can ask.

[0013] Next, phenol novolak mold cyanic-acid ester is mixed to the prepolymer A obtained above, and it is temperature. Stirring mixing is carried out in 100 - 180 **, and cyanic-acid ester Co-op REPORIMA (it is described as "the KOPURE polymer B" below) is manufactured by 3 quantification reactions of a cyanate group. if the conversion of a cyanate group becomes high too much here -- three-dimension bridge formation -- a solvent -- it becomes insoluble and cannot be used as a KOPURE polymer of this invention. Therefore, cyanate group (the residual cyanate group of Prepolymer A, and cyanate group of phenol novolak mold cyanic-acid ester) It is necessary to make a solvent suspend a reaction with meltable conversion. Although it cannot generally ***** since it changes with the classes of the prepolymer A to be used and phenol novolak mold cyanic-acid ester as this conversion, it is 10 - 60% of the cyanate group generally contained at the time of mixing, and 20 - 50% is suitable. In addition, the catalyst shown by manufacture of Prepolymer A on the occasion of manufacture of a KOPURE polymer can be used similarly if needed.

[0014] Moreover, the mixed ratio of Prepolymer A and phenol novolak mold cyanic-acid ester has so high that the content of phenol novolak mold cyanic-acid ester is high the thermal resistance in the last hardened material, although suitably chosen by the thermal resistance for which it asks. However, when the resistance of PCT which is the deterioration test of the resin under elevated-temperature humidification has the too high content of phenol novolak mold cyanic-acid ester, it will fall. Therefore, as a content of desirable phenol novolak mold cyanic-acid ester, it is 10 - 80% and 25 - 75% is suitable.

[0015] Cyanic-acid ester Co-op REPORIMA of this invention manufactured above (KOPURE polymer B) It is independent and can be suitably used combining various resin according to the object and an application. The KOPURE polymer B can be dissolved and used for an organic solvent with a solid. Generally a well-known organic solvent can be used for a solvent. Specifically, ester, such as ketones; propylene-glycol-monomethyl-ether acetate, such as aromatic hydrocarbon; acetones, such as toluene and a xylene, and a methyl ethyl ketone, is suitable.

[0016] As resin to combine, polymerization nature double bond content monomer; polyfunctional maleimide; polyimide; epoxy resins [, such as vinyl compound; unsaturated polyester,], such as Pori allyl compound; N-vinyl-2-pyrrolidones, such as acrylic ester (meta); diaryl benzene and diaryl terephthalate, and a divinylbenzene, etc. can be mentioned.

[0017] If an epoxy resin is suitable and it illustrates concretely in using for laminates especially The product made from oil-ized Shell, Epicoat 1009, 1031, Dainippon Ink & Chemicals, Inc. make, Epiclon N-3050, N-7050, Dow Chemical Co. make, DER-642U and DER-673MF etc. -- bisphenol A mold epoxy resin; -- Tohto Kasei Co., Ltd. make ST-2004 and ST-2007 etc. -- hydrogenation bisphenol A mold epoxy resin; -- the Tohto Kasei Co., Ltd. make -- YDF-2004, the bisphenol female mold epoxy resin of YDF-2007 grade; The Tohto Kasei Co., Ltd. make, YDB-600, YDB-715, the Dow Chemical Co. make, and DER-515 etc. -- bromination bisphenol A mold epoxy resin; -- the Nippon Kayaku Co., Ltd. make -- EPPN-201, EOCN-1020, the Sumitomo Chemical Co., Ltd. make, ESCN-220F etc. -- novolak mold epoxy resin; -- the Nippon Kayaku Co., Ltd. make -- Bromination novolak mold epoxy resins, such as BREN; The Dainippon Ink & Chemicals, Inc. make, Epiclon The novolak mold epoxy resin of bisphenol A of N-880 grade; [Dainippon Ink & Chemicals, Inc. make,] Epiclon The rubber modified epoxy resin of TSR-601 grade; [Nippon Kayaku Co., Ltd. make,] EBPC-200, the Dainippon

Ink & Chemicals, Inc. make, and Epiclone EXA-1514 etc. -- bisphenol smooth S form epoxy resin; -- the Nippon Oil & Fats Co., Ltd. make -- BUREMMA Diglycidyl terephthalate, such as DGT; The product made from Nissan Chemistry, Triglycidyl isocyanurate, such as TEPIC; The product made from oil-ized Shell, YX-4000, the bisphenol mold epoxy resin of YL-6056 grade; The Daicel Chemical Industries, Ltd. make, SEROKI side 2021 etc. -- cycloaliphatic-epoxy-resin; -- the product made from Nippon Steel Chemistry, and ESN-100 etc. -- naphthalene system epoxy resin; -- the Nippon Kayaku Co., Ltd. make and EPP-500 etc. -- the polyfunctional epoxy resin which has a special frame is mentioned.

[0018] a mixing ratio with the resin which the above combines with the KOPURE polymer B of this invention -- although suitably chosen by the application and object about a rate, when it combines with an epoxy resin, generally, 10 - 80% has the desirable content of the KOPURE polymer B, and 20 - 60% is suitable. Moreover, to a resin constituent, various additives, such as a well-known inorganic or organic bulking agent, a color, a pigment, a thickener, lubricant, a defoaming agent, a coupling agent, a photosensitizer, an ultraviolet ray absorbent, and a flame retarder, can be added by request.

[0019] Although it is possible to also make it harden by heating itself, the constituent of this invention can add a heat-curing catalyst in order to make a cure rate quick and to improve workability, profitability, etc. A heat-curing catalyst can add the thermal polymerization catalyst of the cyanate group of the KOPURE polymer B besides adding a catalyst well-known as a heat-curing catalyst for resin to combine. When the thermal polymerization catalyst of a cyanate group is illustrated, it is metal salt; triethylenediamines, such as organometallic compound; aluminum chlorides, such as octylic acid zinc, tin octylate, dibutyl tin dimaleate, and iron <3> acetylacetonate, tin chloride, and a zinc chloride, dimethyl benzylamine, and 2. - Amines, such as a methyl imidazole; phenols, such as a phenol and a catechol, etc. are mentioned and, generally a well-known thing can be used as a curing catalyst of cyanic-acid ester. Although it cannot generally specify from changing with classes of catalyst as an amount of the catalyst which can be added, generally 2% or less is enough. A heat-resistant high hardened material is obtained rather than the constituent with which the constituent which combined the KOPURE polymer B of this invention with the above-mentioned epoxy resin and the additive combined bisphenol A mold cyanic-acid ester or Prepolymer A with the same epoxy resin and the same additive. Also under an elevated temperature, the thermal resistance said here is that the retention of viscoelasticity is high, and is the following phenomena.

[0020] Generally, although thermoplastics changes to the fluid matter above the melting point, the melting point from which thermosetting resin becomes a fluidity does not exist. However, since heat-resistant low thermosetting resin is rubber-ized under an elevated temperature and viscoelasticity falls, the property as resin will fall. On the other hand, also under an elevated temperature, heat-resistant high thermosetting resin is maintaining high viscoelasticity, and is a phenomenon with little property lowering as resin.

[0021] Next, it is mentioned as a description of the constituent using the KOPURE polymer B of this invention that PCT thermal resistance is high. PCT investigates whether resin deteriorates in hydrolysis etc., when a resin hardened material is left under the steamy ambient atmosphere of 121 degree C, and it serves as a rule of thumb which measures the stability of resin. It is known that the constituent which combined the prepolymer (prepolymer A) and epoxy resin of the bisphenol A mold cyanic-acid ester currently incidentally used as a laminate generally has comparatively high PCT thermal resistance. However, as a result of examination of this invention person, the constituent which replaced cyanic-acid ester with phenol novolak mold cyanic-acid ester had the very low PCT heatproof, although thermal resistance was high. That is, the good constituent of PCT thermal resistance came to be obtained with a high heatproof by using the KOPURE polymer of this invention.

[0022] The KOPURE polymer B of this invention is guessed as follows, although many unknown points cannot assert about the exact structure and hardening behavior about a factor with high PCT thermal resistance with a high heatproof. As a cause by which the hardened material of cyanic-acid ester generally shows high thermal resistance, since hardening reactions are 3 quantification reactions of a cyanate group, it says because the triazine ring generated at the time of that crosslinking density is high and hardening is thermally stable. Therefore, when the cyanic-acid ester of many organic functions

shows high thermal resistance with the relation of crosslinking density and mixes the cyanic-acid ester of two organic functions and many organic functions rather than the cyanic-acid ester of two organic functions, middle thermal resistance is shown.

[0023] However, when the cyanic-acid ester of many organic functions is added and a polymerization is further carried out after prepolymer-izing the cyanic-acid ester of two organic functions to the beginning which is the approach of this invention, even if crosslinking density is small by taking the structure which polyfunctional cyanic-acid ester combined with the end of 2 organic-functions cyanic-acid ester prepolymer which spread in the radial, and taking a gestalt like a big network as a whole, it is thought that high thermal resistance is shown. Moreover, about a factor with high PCT thermal resistance, in order to harden so that the resin which combines the hardened material of a reticulated cyanic-acid ester KOPURE polymer may wrap in, having checked penetration of the water molecule to the joint radical which is easy to hydrolyze is guessed.

[0024] In this invention, the constituent which mixes other resin suitable for the target application to the KOPURE polymer B, and is obtained is usually dissolved in a solvent, liquefied resin (it is described as a "varnish" below) is adjusted, impregnation of this varnish is carried out to a reinforcement base material, it is heated suitably, and the prepreg of this invention is manufactured by drying.

[0025] As for the prepreg to manufacture, it is desirable to prepare so that the content of the resin (resin solid content) which sank in may become 25 - 90% of the weight. When the amount of resin is insufficient for the resin in the inside of a base material at less than 25 % of the weight and it is made a laminate, adhesion with both prepregs, prepreg, and copper foil is not obtained, quality becomes instability, and the activity as an application of a printed wired board is not borne. When the amount of resin exceeds 90%, dispersion in the thickness of prepreg becomes large and a possibility that dispersion may arise is in the electrical property of the manufactured printed wired board.

[0026] Especially as a reinforcement base material, although not limited, organic base materials, such as inorganic base material; polyamide nonwoven fabrics, such as glass fabrics and a nonwoven glass fabric, and a liquid crystal polyester nonwoven fabric, etc. are mentioned. Moreover, as for a base material, it is desirable to use what pretreated because of the improvement in adhesion with a base material and resin. As pretreatment, the Nonion system thermal-resistance surfactant processing of coupling agent processing of plasma treatment, corona treatment, a silane coupling agent, a titanate coupling agent, etc., a fluorochemical surfactant, etc. is illustrated, and it can be used, combining suitably.

[0027] Metallic foils, such as copper foil, can be further put on these one side or both sides, and a metallic foil tension laminate can be obtained for the prepreg obtained as mentioned above a need number-of-sheets pile and by carrying out heating pressing of this. Generally heating application-of-pressure conditions are temperature, although it changes with classes of resin compounded with a base material. They are 10-30kg/cm² and time amount preferably 170-230 ** and the pressure of 10-50kg/cm². 40-120 It is desirable to set it as a part. Using the manufactured metallic foil tension laminate, a printed wired board can be manufactured by the well-known approach, and a multilayer printed wiring board can be further manufactured by carrying out multilayering laminate molding of the metallic foil to prepreg in piles. The printed wired board manufactured using the resin constituent containing the KOPURE polymer B of this invention has high thermal resistance, there are no problems, such as deformation by the heat history in multilayering laminate molding, and a reliable multilayer board is obtained.

[0028]

[Example] Although an example and the example of a comparison are used for below and this invention is explained to it still more concretely, this invention is not limited to below. In addition, the weight section is expressed unless it refuses especially the "section" and "%" through an example and the example of a comparison. The measured value in an example and the example of a comparison is also having measured using the following equipment and approaches.

[0029] - Conversion of a cyanate group : he is Bio-Rad as infrared spectrometer (IR). Made in Laboratory, model It measured using FTS175C (=FT-IR). The cyanate group was made into the peak intensity of 2270cm⁻¹, and set the N0 and prepolymer-izing back to N1 for initial value. The benzene

ring was made into the peak intensity of 1500cm⁻¹, set the A0 and prepolymer-izing back to A1, and computed initial value by the following formula.

Measurement of cyanate-group conversion (%) = $(N0/A0 - N1/A1) / (N0/A0) \times 100$ and molecular weight: He is Shimadzu as GPC (gel PAMI nation chromatography). LC-10-GPC system (column 801,802,803) It uses and is an expansion solvent tetrahydrofuran (THF). It measured.

[0030] Example 1 bisphenol A mold cyanic-acid ester (a 2[=2 and]-bis(4-SHIANATO phenyl) propane, a trade name: describe it as "BPA-CN" sky REXX CA200, the Mitsubishi Gas Chemical Co., Inc. make, and the following) It is temperature about the 1,000 sections. With 135 - 145 ** It was made to react for 6.5 hours and the prepolymer of bisphenol A cyanic-acid ester was obtained. the obtained prepolymer -- GPC the result of the measurement to depend -- number average molecular weight (Mn) 1,570 and weight average molecular weight (Mw) 5,460 and Mw/Mn=3.5 it was . Moreover, FT-IR As a result of analyzing, it is cyanate group conversion. It was 61% of matter (it is described as "A1" below).

[0031] To the prepolymer A1 500 section manufactured above, it is phenol novolak mold cyanic-acid ester (they are considerable and LONZA to trade name ;P T-30, number-average-molecular-weight 615, and average abbreviation 4.7 of the cyanate group contained in 1 molecule it is described as "PT-30" shrine make and the following). The 500 sections are added and it is temperature. With 130 - 145 ** It was made to react for 3 hours. obtained KOPURE polymer the result analyzed by GPC and IR -- Mn=1,870 and Mw/Mn=5.8 it is -- it was the matter to which 22% of the cyanate group at the time of mixing reacted (it is described as "B1" below). The GPC chart of the KOPURE polymer B1 was shown in drawing 1.

[0032] the same approach as example 2 example 1 BPA-CN while performing prepolymer-ization and supervising by IR and GPC -- reaction temperature 130degree-C-145 ** -- it reacts for 4 hours -- making -- Mn=795, Mw/Mn=3.2, and cyanate group conversion 43% of prepolymer was obtained (it is described as "A2" below).

[0033] To the prepolymer A2 500 section manufactured above, it is phenol novolak mold cyanic-acid ester (they are considerable and LONZA to trade name ;P T-15, number-average-molecular-weight 443, and average abbreviation 3.3 of the cyanate group contained in 1 molecule it is described as "PT-15" shrine make and the following). The 500 sections are added and it is temperature. With 130 - 145 ** It was made to react for 5 hours. obtained KOPURE polymer the result analyzed by GPC and IR -- Mn=2,120 and Mw/Mn=5.3 it is -- it was the matter to which 31% of the cyanate group at the time of mixing reacted (it is described as "B-2" below).

[0034] It used for the prepolymers A1 or A2 manufactured in the three to example 5 examples 1 and 2 in the examples 1 and 2. PT-30 and PT-15 It added by the ratio indicated to a table 1, KOPURE polymer-ization was performed by the same approach as an example 1, and the KOPURE polymer was obtained (the obtained KOPURE polymer is hereafter described as B3 - B5, respectively). The result was combined with examples 1 and 2 and was shown in a table 1.

[0035] To the prepolymer A1 100 section manufactured in the example of comparison 1 example 1, it is phenol novolak mold cyanic-acid ester (they are considerable and LONZA to trade name ;P T-60, number-average-molecular-weight 744, and average abbreviation 5.6 of the cyanate group contained in 1 molecule shrine make). The 100 sections are added and it is temperature. It was made to react in 130 - 145 **. When reaction-time 2 hours passed, rapid viscosity lifting broke out, and it became insoluble gel at the solvent.

[0036] It is the same in having used in the example of comparison 2 example 1. BPA-CN The 500 sections and PT-30 With temperature 135 - 145 ** after mixing the 500 sections It was made to react for 5.5 hours and the KOPURE polymer (it is described as "C2" below) was manufactured. KOPURE polymer C2 As a result of analyzing by GPC and IR, they are Mn=1,420, Mw/Mn=19.9, and cyanate group conversion. It was 42%. The GPC chart of the KOPURE polymer C2 was shown in drawing 2 . If drawing 1 is compared with drawing 2 , at the KOPURE polymer C2 of drawing 2 , it is degree of dispersion (Mw/Mn) to the low-molecular-weight object whose molecular weight the KOPURE polymer B1 of drawing 1 is a set and a monomer comparatively hardly being seen. It is large, there are also many high molecular weight objects, and it turns out that many monomers also exist.

[0037] The PT-30 [same] as having used in the example of comparison 3 example 1 It is temperature about the 500 sections. It is made to react in 130 - 145 ** for 2 hours, and is a prepolymer. (it is described as "C3" below) It obtained. obtained prepolymer C3 the result analyzed by GPC and IR -- Mn= -- 1, 070, Mw/Mn=10.2, and cyanate group conversion It was 19%. The result of the examples 1-3 of a comparison was shown in a table 2.

[0038]

[A table 1]

Example 1 Example 2 Example 3 Example 4 Example 5 prepolymer A A1 A2 A1 A2 A1 cyanate-group conversion 61 43 61 43 61 Phenol novolak PT-30 PT-15 PT-30 PT-30 PT-15 Mold cyanic-acid ester a mixing ratio -- *1 50/50 50/50 70/30 30/70 40/60 Reaction time (hrs) 3 53 3 6 Cyanate group conversion 2231 1525 36 number average molecular weight (Mn) 1,870 2, 1201, 5701, 4801, 950 degree of dispersion (Mw/Mn) 5.6 5.3 5.8 4.8 5.9 KOPURE polymer sign B1 B-2 B3 B4 B5 notes -- *1 : A mixing ratio is a weight ratio of prepolymer A / phenol novolak mold cyanic-acid ester.

[0039]

[A table 2]

Example 1 of a comparison Example 2 of a comparison Example 3 of a comparison Prepolymer A A1 BPA-CN - Phenol novolak PT-60 PT-30 PT-30 Mold cyanic-acid ester a mixing ratio -- *1 50/50 50/50 0/100 reaction time (hrs) 2.5 7.5 3 Cyanate group conversion - 42 27 number average molecular weight (Mn) Gelation 1,420 1,070 Degree of dispersion (Mw/Mn) - 19.9 10.2 KOPURE polymer sign - C2 C3 notes -- *1 : A mixing ratio is a weight ratio of Prepolymer A, or BPA-CN / phenol novolak mold cyanic-acid ester.

[0040] the 1 KOPURE polymer B30 section obtained in the example 6 example 1, and an epoxy resin 1 (trade name: -- ESCN-220F --) it is described as "ESCN-220F" the Sumitomo Chemical Co., Ltd. make and the following -- the 50 sections and an epoxy resin 2 (trade name: -- Epicoat 828 and the product made from oil-ized Shell --) it is described as "Epicoat 828" below -- the 20 sections -- methyl ethyl ketone the 200 sections -- dissolving -- as a catalyst -- octylic acid zinc 0.01 The section was added and the varnish was adjusted. this varnish -- thickness it sinks into 100-micrometer glass fabrics, and dries -- the gelation time in 170 degree C 150 seconds B-stage prepreg was obtained. this prepreg electrolytic copper foil (3EC, Mitsui Mining and Smelting Co., Ltd. make) with a thickness of 18 micrometers is arranged on a four-sheet pile and both sides -- press forming was carried out on 200 degree C, 20 kg/cm², and the conditions of 2 hours, and double-sided copper clad laminate was obtained. The property of this copper clad laminate was shown in a table 4.

[0041] Measurement of viscoelasticity is Rheometrics. It measured by the following approaches using the rheometer of a shrine. Resin powder which bent and took out the above-mentioned prepreg The hardening reaction was carried out on 200 degrees C and the conditions of 2 hours. This hardened material After cooling to 100 degrees C, they are the programming rate of 2 degrees C / min. Viscoelasticity measurement to 280 degrees C was performed. The change behavior of the viscoelasticity by temperature was shown in drawing 3. Moreover, the viscoelasticity value of 150 degree C and 260 degrees C was shown in a table 4.

[0042] According to seven to example 13 example 6, the varnish was prepared by the presentation shown in a table 3, prepreg was created, and copper clad laminate was manufactured. The result of having measured viscoelasticity in the list as a result of measuring the property of the manufactured copper clad laminate was shown in a table 4.

[0043] It replaced with the KOPURE polymer B1 of example of comparison 4 example 6, and the varnish was adjusted by the same presentation as an example 6 using the prepolymer A1 of an example 1. Prepreg was created like the example 6 and the result of having performed assessment by copper clad laminate and viscoelasticity measurement was shown in a table 4 and drawing 4.

According to the example 5 of a comparison, and six examples 6, the varnish was prepared by the presentation shown in a table 3, prepreg was created, and copper clad laminate was manufactured. The result of having measured viscoelasticity in the list as a result of measuring the property of the manufactured copper clad laminate was shown in a table 4.

[0044]

[A table 3]

An example The example of a comparison A presentation component 6 7 8 9 10 11 12 13 4 5 6
 KOPURE polymer B1 30 40 20 KOPURE polymer B-2 30 50 The KOPURE polymer B3 30 KOPURE
 polymer B4 30 KOPURE polymer B530 KOPURE polymer C2 30 The KOPURE polymer C3 30
 Prepolymer A1 30ESCN-220F 50 50 20 20 50 30 20 70 60 50 60 Epicoat 82820 10 30 10 30 10 20
 10 Epicoat 1001 YX4000 20 10 BREN 30 2010 notes ESCN-220F : Cresol novolak mold epoxy resin
 Epicoat 828 1001: The bisphenol A mold epoxy resin YX 4000:4, 4'-diglycidyl oxy-- 3, 3', 5, 5'-
 tetramethyl - 1 1'-BIFE nil BREN : Bromination phenol novolak mold epoxy resin [0045]

[A table 4]

Example & Copper foil adhesive strength Heat-resistant *1 Moisture absorption solder PCT thermal
 resistance Example No of a comparison (kN/cm²) 150 degrees C 260 degrees C Thermal resistance A
 fruit 6 1.1 2.63 1.35 10/10 Have no change. **7 1.0 2.55 1.38 10/10 Have no change. **8 1.1 2.61 1.55
 with no 10/10 change -- **9 1.2 2.48 1.25 10/10 Change-less **10 1.1 2.54 1.65 10/10-change-less
 **11 1.2 2.65 1.699/10 It is discoloration **12 slightly. 1.1 2.68 1.59 7/10 It discolors slightly. **13 1.2
 2.41 1.19 10/10 with no change a ratio -- 4 1.1 2.43 0.9210 / 10 change nothing **5 0.8 2.45 1.21 5/10
 Discoloration **6 0.8 2.58 1.562/10 Discoloration and bulging *1 : The viscoelasticity by the
 rheometer, unit x10⁷ P.

[0046] Measurement of a physical-properties value was performed by the following approach.

Copper foil adhesive strength : JIS (C6481) It carried out by being based.

heat-resistant *1 : resin powder is stiffened by the approach indicated in the example 6 -- the value of
 the viscoelasticity in 150 degree C and 260 degrees C was measured. A unit is x10⁷P.

Moisture absorption pewter thermal resistance : Test piece of copper clad laminate (5x5cm) It was
 immersed in the 260 degree-C pewter bath after making it absorb moisture on PCT conditions (121
 degrees C, two atmospheric pressures) for 10 hours, and the existence of exfoliation of copper foil was
 observed. The result indicated the number of sheets which passed with the test piece of ten sheets.

PCT thermal resistance : Overall etching of the copper clad laminate was carried out, copper foil was
 removed, and the test piece of a laminate was created. Test piece Under the ambient atmosphere of the
 steam of PCT conditions (121 degrees C, two atmospheric pressures) It was left for 500 hours and the
 appearance of a test piece was observed visually.

[0047] Prepreg produced in the example 14 example 7 Use four sheets, and electrolytic copper foil (the
 product made from Mitsui Mining & Smelting , 3EC) with a thickness of 35 micrometers is used as
 copper foil, and also it is the thickness of an insulating layer like an example 6. 0.4mm double-sided
 copper clad laminate was manufactured. This double-sided copper clad laminate to 510x405mm The
 angle was started and the inner strake was manufactured by using a dry film resist, exposing the printed-
 circuit pattern for inner layers, developing negatives, and etching. In this circuit pattern, it is the
 direction of X as a reference point for dimensional change measurement. 500mm, the direction of Y The
 point with spacing of 400mm has been arranged. Multilayering laminate molding of 1 sheet ** *****
 and the 35-micrometer still more nearly same electrolytic copper foil was carried out for the prepreg of
 the obtained inner strake produced in the example 7 on the same conditions in piles up and down, and 4
 lamellaes of double-sided copper foil were manufactured. As a result of carrying out coordinate
 measurement of the reference point for dimensional change measurement arranged to the inner layer of
 these 4 lamellaes, a dimensional change is direction =+of X 100. mum, the direction of Y = it was +70
 micrometers.

[0048] In example of comparison 7 example 14, the prepreg produced in the example 4 of a comparison
 as prepreg was used, and also it was made the same. As a result of carrying out coordinate measurement
 of the reference point for dimensional change measurement arranged to the inner layer of 4 obtained
 lamellaes, a dimensional change is direction =+of X 300. mum, the direction of Y = +150 It was mum.

[0049]

[Effect of the Invention] Cyanic-acid ester Co-op REPORIMA which prepolymer-ize 2 organic-
 functions cyanic-acid ester, and polyfunctional cyanic-acid ester is made to add and react to this, and is

obtained can obtain a hardened material with little [even if it mixes with other resin and hardens, there is little heat-resistant lowering, and] resin degradation especially under elevated-temperature humidification. Therefore, the cyanic-acid ester KOPURE polymer of this invention is resin which can be used effective in the various applications for which a severe condition is needed.

[Translation done.]

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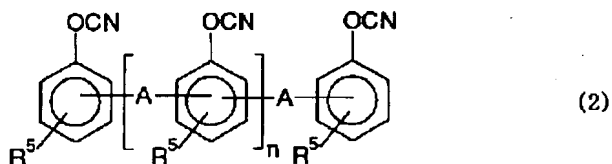
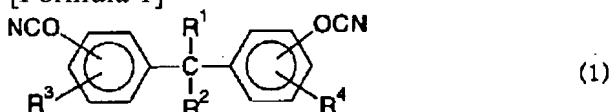
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CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1) The following general formula after prepolymer-izing 2 organic-functions cyanic-acid ester shown (2) Cyanic-acid ester Co-op REPORIMA obtained by adding the polyfunctional cyanic-acid ester shown and prepolymer-izing further.

[Formula 1]



(In a formula (1), you may differ, it is that R1 and R2 are the same, or a hydrogen atom, a straight chain, a with a branched carbon number of six or less alkyl group or the cycloalkyl that R1 and R2 combined, and R3 or R4 are a hydrogen atom, a halogen atom, a straight chain, or the with a carbon number of six or less branched alkyl group.) Formula (2) It sets and is n. 0.5-3 A positive number is expressed, R5 is a hydrogen atom, a halogen atom, a straight chain, or the with a carbon number of six or less branched alkyl group, and A is a methylene group or a dicyclopentadienyl radical.

[Claim 2] This general formula (1) 2 organic-functions cyanic-acid ester shown is bisphenol A mold cyanic-acid ester, and it is this general formula (2). Cyanic-acid ester Co-op REPORIMA of the ***** 1 publication whose polyfunctional cyanic-acid ester shown is phenol novolak mold cyanic-acid ester.

[Claim 3] This general formula (2) Cyanic-acid ester Co-op REPORIMA according to claim 1 whose amount of the polyfunctional cyanic-acid ester used shown is 30 - 60% of cyanic-acid ester Co-op REPORIMA.

[Claim 4] This general formula (1) Cyanic-acid ester Co-op REPORIMA according to claim 1 which is the thing to which 20 - 60% of the cyanate group contained in raw material cyanic-acid ester makes prepolymer-ization of 2 organic-functions cyanic-acid ester shown come to react.

[Claim 5] This general formula (1) To the prepolymer of this 2 organic-functions cyanic-acid ester shown, it is this general formula (2). Cyanic-acid ester Co-op REPORIMA according to claim 1 which is the thing to which 10 - 50% of the cyanate group in which prepolymer-ization performed by adding the polyfunctional cyanic-acid ester shown exists in the condition of having added is made to react.

[Claim 6] The thermosetting resin constituent which comes to combine the resin in which cyanic-acid ester Co-op REPORIMA and heat curing according to claim 1 are possible.

[Claim 7] The thermosetting resin constituent according to claim 6 whose resin in which this heat curing

is possible is an epoxy resin.

[Claim 8] Prepreg which comes to carry out impregnation and desiccation of the thermosetting resin constituent according to claim 6 at a reinforcement base material.

[Claim 9] The metallic foil tension laminate which comes to carry out laminate molding of prepreg and a metallic foil according to claim 8.

[Translation done.]